Synthesis and Characterization New Polymerizable Liquid Crystal Monomer and its Atom Transfer Radical Polymerization for Novel Side Chain Liquid Crystalline Polymers

By:

M.R.K. Sheikh, Satoshi Masuyama, Masatoshi Tokita
and
Junji Watanabe

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SYNTHESIS AND CHARACTERIZATION NEW POLYMERIZABLE LIQUID CRYSTAL MONOMER AND ITS ATOM TRANSFER RADICAL POLYMERIZATION FOR NOVEL SIDE CHAIN LIQUID CRYSTALLINE POLYMERS.

M. R. K. Sheikh*[a], Satoshi Masuyama[b], Masatoshi Tokita[b] and Junji Watanabe[b]
[a]Department of Chemistry, Faculty of Science, University of Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia.
[b]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

We synthesized a new polymerizable liquid crystal (LC) monomer, which contain naphthalene ring in the mesogen. The new LC monomer was characterized by ^{1}H NMR, Polarized Optical Microscope (POM), Differential Scanning Calorimeter (DSC) and Wide Angle X-ray Diffractometer (WAXD) measurements. Living Atom Transfer Radical Polymerization (ATPR) was used to synthesize side chain liquid crystalline polymers (SCLCPs) of different molecular weight. The SCLCPs were characterized by ^{1}H NMR, Gel Permeation Chromatogram (GPC), POM, DSC and WAXD. The SCLCPs showed isotropization at 179 °C, a very wide range nematic phage appeared from177-117 °C temperature region and smetic A phage appeared at or below 117°C. The glass transition temperature (*Tg*) was increased with the increase of molecular weight (M_n) of SCLCPs.

Keywords: LC Monomer, ATRP, Novel SCLCPs, Wide temperature rage nematic phage and Smetic A phage.

Introduction

Side-chain liquid crystalline polymers (SCLCPs) represent a combination of liquid crystalline behavior and polymeric properties. SCLCPs consist of a polymer backbone attached through some flexible hydrocarbon 'spacers" to liquid crystal mesogenic groups in the side chain to form a comb-like structure. Such polymers are of considerable interest as potential material for a variety of applications in physical optics and display technology, especially in relation to reverse information storage devices [1-5]. Most of the studies reports the SCLPs to date have been concern with materials in which the mesogenic unit contains only phenyl or biphenyl groups [6-15]. In this report, we will describe the synthesis and characterization of new polymerizable LC monomer, which conations naphthalene ring in the mesogen. The powerful method of polymerization i.e., atom transfer radical polymerization (ATRP) was used to polymerize the new monomer for obtaining novel SCLCPs. ^{1}H NMR (Nuclear Magnetic Resonance), GPC (Gel Permeation Chromatography), POM (Polarized Optical Microscope), DSC (Differential Scanning Colorimetry) and WAXD (Wide Angle X-ray Diffractometer) were used to characterize the new monomer and synthesized SCLCPs.

Experimental section

Materials. 6-Hydroxy-2-napthaonic acid (Aldrich, 98%), 4-Methoxyphenol (TCI, Japan, 99%), Conc. H_2SO_4 (Yotuhata Pure Chemicals, Japan, 95%), Boric Acid (Sigma-Aldrich, 99.5%), Toluene, dehydrate (Wako, Japan, 99.5%), 1,6-Dibromohexane (Aldrich, 96%), Potassium carbonate (Takahashi Pure Chemicals, Japan, 99%), Acetone (TCI, Japan, 99.5%), Methacrylic acid (Sigma-Aldrich, 99%), Potassium hydrogen carbonate (Wako, Japan, 99.3%), Hydroquinone (TCI, Japan, 99%), Dimethylformamide anhydrous (DMF) (Aldrich, 99.5%),), Chloroform (ShinEtsu, Japan, 99%), Anisole, dehydrate (Aldrich, 99.7%), 2-Bromoisobutyric acid ethyl ester (TCI, Japan, 98%), (-)-Sparteine (Aldrich, 99%), Copper (I) bromide (Wako, Japan, 99.9%), Tetrahydrofuran (THF) (TCI, Japan, 98%).

Measurements. ^{1}H NMR (400 MHz) spectra were recorded in chloroform-d ($CDCl_3$) and dimethyl sulfoxide (DMSO) using tetramethylsilane as internal reference ($\delta = 0$) on a JEOL EX– 400 spectrometer.

The number average molecular weight (M_n) and polydispersity (M_w/M_n) of synthesized polymer was measured by gel permeation chromatography (GPC) on a Jasco Gulliver System (PU-986, CO-1560, UV975, Shodex IR-72) equipped with a series of PS gel columns (Shodex GPC K-2004), molecular weight range up to 2.1×10^5, flow rate 3 mL/min, using chloroform as an eluent at 40 °C with a PS standard.

The texture at different phase of synthesized monomer and polymers were obtained using an Olympus BX50 Polarized Optical Microscope (POM) fitted with Mettler Toledo FP90 Central Processor and FP82HT Hot Stage. The images were recorded on Olympus Digital Camera.

Differential Scanning Calorimetric (DSC) measurements were carried out on a Perkin-Elmer Pyris 1 thermal analysis system and a Perkin-Elmer Thermal Analysis Controller TAC 7/DX. The samples were hermetically sealed in aluminum pans and scanned under N_2 at the temperature range from -50 to 250 °C with heating rates of 10 °C min^{-}1.

Wide Angle X-ray Diffraction (WAXD) patterns of LC monomer and polymers were obtained at different temperature by Rigaku RINT 2000 X-ray generator. A 100-μm resolution, 1150×1150 pixel imaging plate (HR-V, Fuji Film Co., Ltd.) was exposed to the scattered x-ray beam, and then scanned by an R-AXIS-DSBC data reader. Mettler Toledo Hot Stage was used to control the temperature. The obtained digital data were stored and analyzed by computer software.

Synthesis of LC Monomer M-1 (see scheme-1).

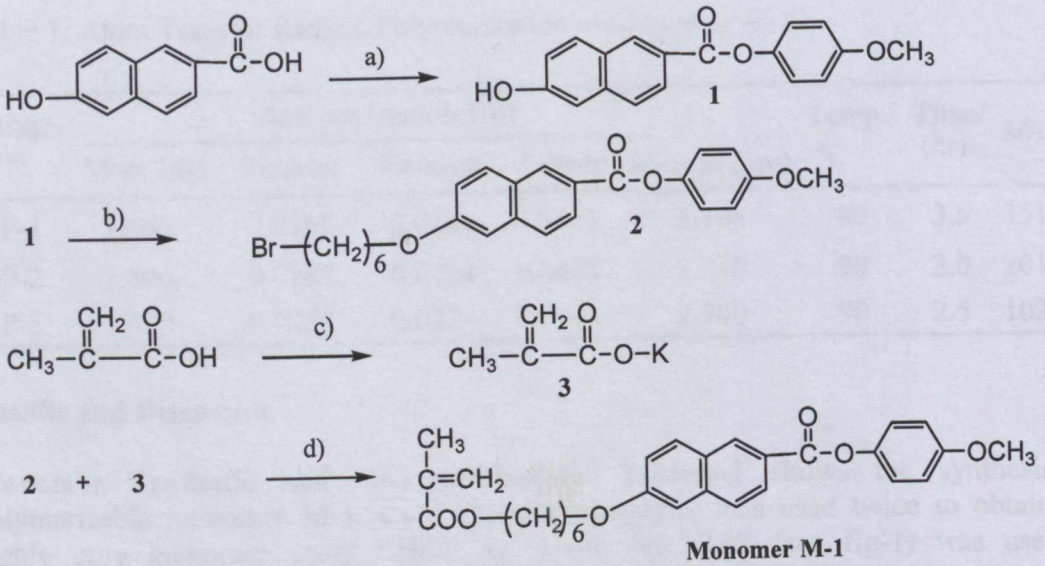
a) **Synthesis of 4-methoxyphenyl 6-hydroxynaphthalene-2-carboxylate (1):** Van Meter (6) process was modified to synthesize this compound and the modification process is as follows. To a suspension of *p*-methoxyphenol (25 gm, 0.214 mole) and *p*-hydroxynapthaonic acid (33.87 gm, 0.18 mole) in dehydrate toluene concentration sulfuric acid (0.9 gm) and boric acid (0.5 gm, 6% mole) were added. The reaction was heated under reflux for 72 h using a Dean-Strak-trap. The solvent was then removed at reduced pressure and the product was washed with petroleum ether/ hexane (1:1) mixture. 100 ml acetonitrile was added into the reaction mixture and heated at 50 °C and again added 200 ml $CHCl_3$ into the mixture, and

kept stand for 1 h. There were two types of particles floated into $CHCl_3$. The big size particles were product and separated by filtration with 200-mesh screen. The separated big size particles were dissolved in THF and concentrated by vacuum distillation. 10-fold excess methanol was added into the concentrated solution of product. The solid impurities were removed by filtration. The pure product was obtained by removing methanol from the solution by vacuum evaporation. The pure product was 18.0 gm and yield was 34.0%. ^{1}H NMR of product **1** (DMSO, δ, ppm) 10.3 (H, s, Np-OH), 8.7 (H, s, Np-H), 7.8-8.1 (3H, m, Np-H), 7.2 (4H, m, Ar-H), 7.0 (2H, m, Ph-H), 3.8 (3H, s, Ph-OCH_3).

b) **Synthesis of 4-methoxyphenyl 6-(6-bromohexyloxy)naphthalene-2-carboxylate (2):** 30.58 mmole (9gm) of 4-methoxyphenyl 6-hydroxynaphthalene-2-carboxylate (**1**) was dissolved in about 70 ml acetone and a small amount of K_2CO_3 was also dissolved in acetone and mixed together. 244 mmole (59.5 gm) of 1,6-dibromohexane (Eight times of compound **1**) was added slowly into the mixture **1**. After complete addition of Br-compound the reaction was heat at reflux (85°C) temperature for 24 hours. The reaction mixture was hot filtered (2 times) and acetone was removed by vacuum evaporation. Petroleum ether and hexane (1:1) mixture was added for precipitation and stand 12 h for perfect precipitation. The product was dried at 40 °C under vacuum. The pure product was 7.3 gm, 15.96 mmole, 52.2% yield. ^{1}H NMR of product **2** ($CDCl_3$, δ, ppm) 8.7 (H, s, Np-H), 7.7-8.2 (3H, m, Np-H), 7.1-7.3 (4H, m, Ar-H), 6.95 (2H, m, Ph-H), 4.15 (2H, m, O-CH_2-), 3.85 (3H, s, Ph-OCH_3), 3.45 (2H, m, -CH_2-Br), 1.8-2.0 (4H, m, -CH_2-), 1.2-1.4 (4H, m, -CH_2-).

c) **Preparation of Potassium methacrylate (3):** 13.4 mmole (1.15 gm) methacrylaic acid was added slowly into 13.3 mmole (1.33 gm) potassium hydrogencarbonate for 5 min. at room temperature to for potassium methacrylate.

d) **Synthesis of LC Monomer M-1**: A solution of 4-methoxyphenyl 6-(6-bromohexyloxy)naphthalene-2-carboxylate (8.96 mmole, 4 gm) and hydroquinone (0.1 mmole, 0.01 gm) in DMF (200 ml) was added slowly into the previously prepared potassium methacrylate solution. The reaction mixture was heated with stirring at 100°C for 24 hours. Solvent was removed under vacuum after complete the reaction and 500 ml water was added at room temperature. The solid was separated by filtration and again dissolved in dichloroethane. The organic phase was washed twice by 5% NaOH solution and twice by H_2O. The solvent was removed by vacuum. The crude product was 3.3 gm and yield was 80%. The crude product (Monomer M-1) was finally purified by column chromatogram using $CHCl_3$ as eluent and the yield was 73%. ^{1}H NMR of product **Monomer M-1** ($CDCl_3$, δ, ppm) 8.7 (H, s, Np-H), 7.7-8.2 (3H, m, Np-H), 7.1-7.3 (4H, m, Ar-H), 6.9-7.0 (2H, m, Ph-H), 6.1 (H, s, =CH_2), 5.6 (H, s, =CH_2), 4.1-4.3 (4H, m, O-CH_2-), 3.85 (3H, s, Ph-OCH_3), 1.95 (3H, s, -CH_3), 1.7-1.9 (4H, m, -CH_2), 1.4-1.6 (4H, m, -CH_2).



Monomer M-1

Reaction conditions:

a) i. *p*-Methoxyphenol, ii. Toluene/ Conc. H_2SO_4, HBO_3 iii. Reflux for 24 hrs with Dean-Strak-Trap

b) i. K_2CO_3/ Acetone, H_2O ii. Br-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-Br

c) i. $KHCO_3$

d) i. Hydroquinone/ DMF ii. 100 °C for 24 hrs.

Atom Transfer Radical Polymerization (ATRP) of Monomer M-1 (7-11): At first the Macromonomer M-1 is added into the polymerization (see table-1 for amount and detail polymerization conditions) ampoule and then added anisole, 2-bromoisobutyric acid ethyl ester, (-)-spartein and copper (I) bromide, anisole as solvent, initiator, ligand and catalyst respectively. The polymerization ample was connected to high vacuum system, degassed at liquid nitrogen temperature three times, and sealed under high vacuum. The polymerization was carried out at 90°C for 3 h. After complete the polymerization was stopped by cooling and the polymerization mixture was diluted with THF. The diluted polymerization mixture was passed through a short column of aluminum oxide (activated, basic, Brockman I), using THF as eluent to remove copper salt. Next it was concentrated by vacuum evaporation and precipitated into 15-fold excess of methanol. The unreacted monomer was removed by overnight soxhlet extraction using methanol. Polymer solution was collected as dichloromethane extraction and the solution was concentrated by vacuum evaporation and finally the pure polymer product was precipitate into large amount of methanol. The complete removal of monomer from the polymer was confirmed by the disappearance of the peaks associated with the alkene protons peaks of monomer from 6.1 and 5.6 ppm (^{1}H NMR). ^{1}H NMR of Polymer ($CDCl_3$, δ, ppm) 8.6 (H, s, Np-H), 7.5-8.0 (3H, m, Np-H), 6.7-7.1 (4H, m, Ar-H), 6.7-7.15 (6H, m, Ph-H and CH_2-), 3.8 - 4.1 (4H, m, O-CH_2-), 3.7-3.8 (3H, s, Ph-OCH_3), 1.7-1.8 (3H, s, -CH_3), 1.3-1.7 (8H, m, -CH_2).

Table 1: Atom Transfer Radical Polymerization of Monomer M-1.

Expt. no	Amount (mmole) of					Temp./ °C	Time/ (hr)	Mn_{GPC}	Mw/Mn
	Mon. M-1	Initiator	Catalyst	Ligand	Solvent (gm)				
P-1	1.680	0.0168	0.0201	0.0403	3.108	90	3.5	35185	1.44
P-2	1.500	0.0187	0.0224	0.0448	2.740	90	3.0	20150	1.32
P-3	1.020	0.0255	0.0224	0.0448	2.740	90	2.5	10230	1.18

Results and Discussion

Monomer Synthesis and Characterization: Scheme-1 shows the synthesis of polymerizable monomer M-1. Column chromatography was used twice to obtain the highly pure monomer using $CHCl_3$ as eluent. ^1H NMR (see fig-1) was used to characterize the new monomer M-1. The LC property of the synthesized monomer was assigned on the basis of their optical microscope textures (fig.2). From the polarized optical microscope (POM) textures (cooling from isotropization temperature, 91.66°C), it can be seen that at 87.4°C, monomer M-1 shows Schlieren texture of nematic phase, at 75.0 °C fan shaped texture of nematic phase, at 37.0°C homotropic texture of Smetic A (SmA) phase ware appeared and very slow crystallization start at 35.5 °C (fig.2). From the DSC measurement (fig.3) it is also observed that the isotropization temperature was 87.2 °C and crystallization temperature was 32.3 °C. The layer space of the SmA (40-37 °C was 27.5 Å measured by Wide Angle X-ray Diffraction (WXRD) and the layer space of smetic phase was also confirmed by the Spartan software (26.6- 27.5 Å).

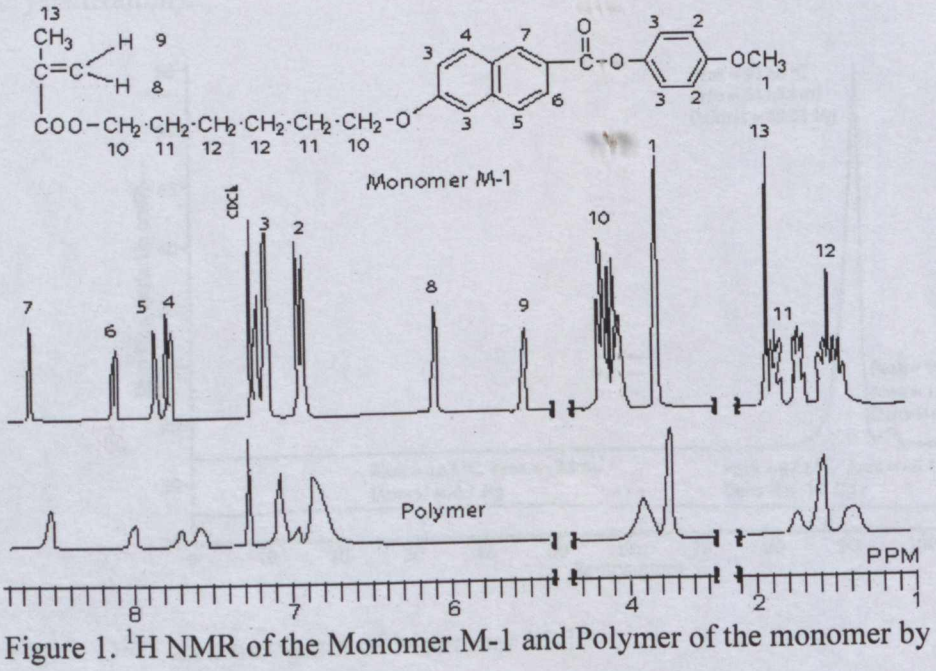


Figure 1. ^1H NMR of the Monomer M-1 and Polymer of the monomer by ATRP.

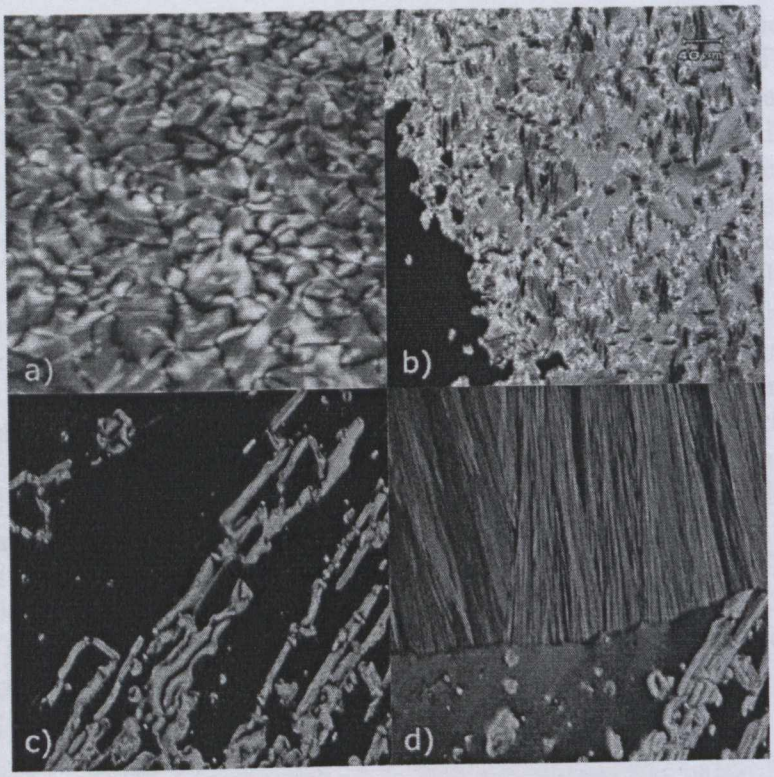


Fig. 2. Polarized Optical Microscopic (POM) textures of Monomer M-1:
a). Schlieren texture of nematic phase at 87.4 °C (cooling from isotropization temperature, 91.66 °C). b). Fan shaped texture of nematic phase at 75.0 °C. c) Homotropic texture of SmA phase at 37.0 °C. d). Crystal at 35.5 °C (slow crystallization).

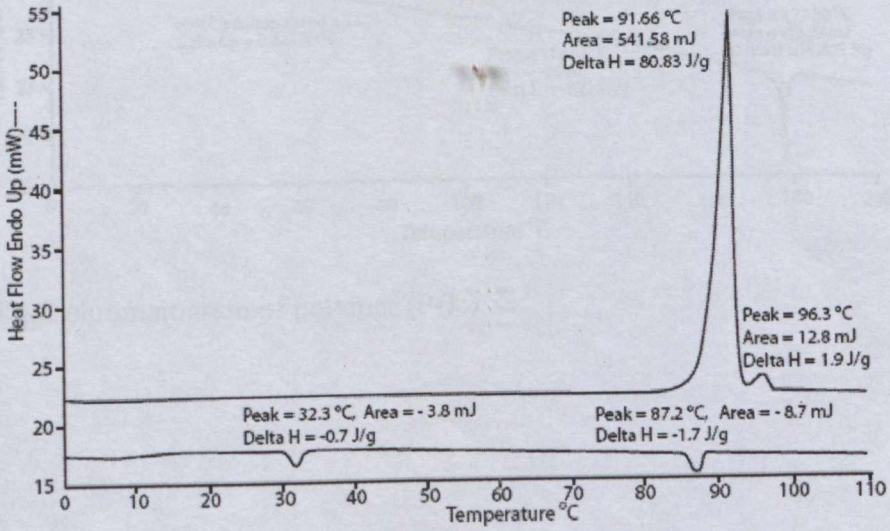


Fig. 3. DSC chromatogram of Monomer M-1.

Characterization of Polymer: The synthesized polymer of new M-1 monomer obtained by ATRP was characterized by ^{1}H NMR, GPC, DSC, POM, and WXRD. The conversion of monomer M-1 into polymer was confirmed by the disappearance of alkene protons peaks of ^{1}H NMR from 6.1 and 5.6 ppm. Polymerization conditions and GPC results are showed in table-1. It is seen from the table-1 that the highest molecular weight was (P-1. 35185) obtained at 1:100 initiator and monomer ratio and the polymerization time was 3.5 hours. The polydispersity of the synthesized polymers were different. The polydispersity of synthesized polymers increases with the increases of molecular weight. This is due to the increase of polymerization time. DSC chromatogram of the polymer (P-1) was shown in figure 4. From the chromatogram is seen that the very wide range nematic phase appeared (178-118 °C) than the normal SCLPs. This probably due to the presence of naphthalene group in the mesogen of LC monomer. Figure 5 shows the POM texture of polymer (P-1) at different temperature (cooling from the isotropic temperature). Nematic phase appeared below isotropic temperature and below 115 °C the Smetic A phage appeared. The nematic and smetic A phage was confirmed by the WAXD image (Fig. 6). There was no layer space at or above 125 °C. The layer space appeared at 100 °C (26.8 Å) and it was almost same at room temperature (26.5 Å). There was no layer space change of smetic phase due to the change of temperature, so the smetic phage of the SCLPS was smetic A phage.

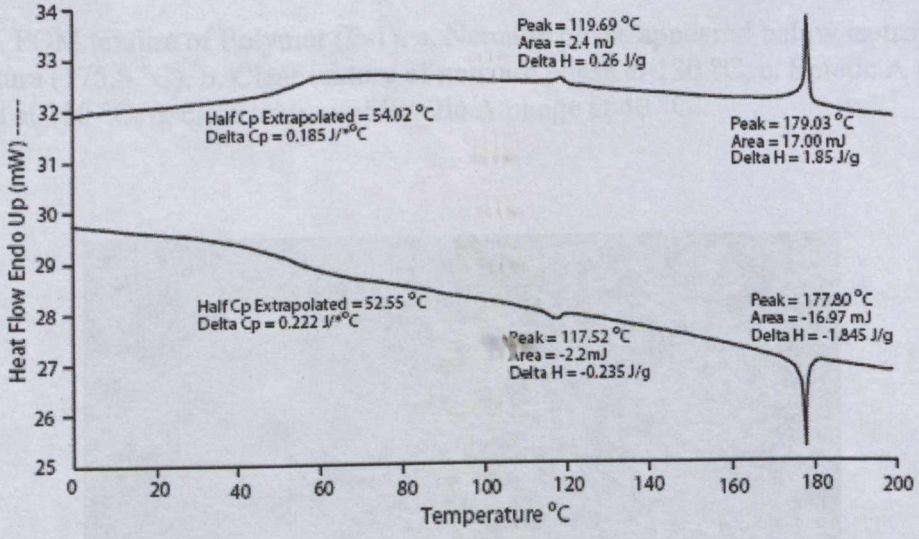


Figure 4. DSC chromatogram of polymer (P-1.).

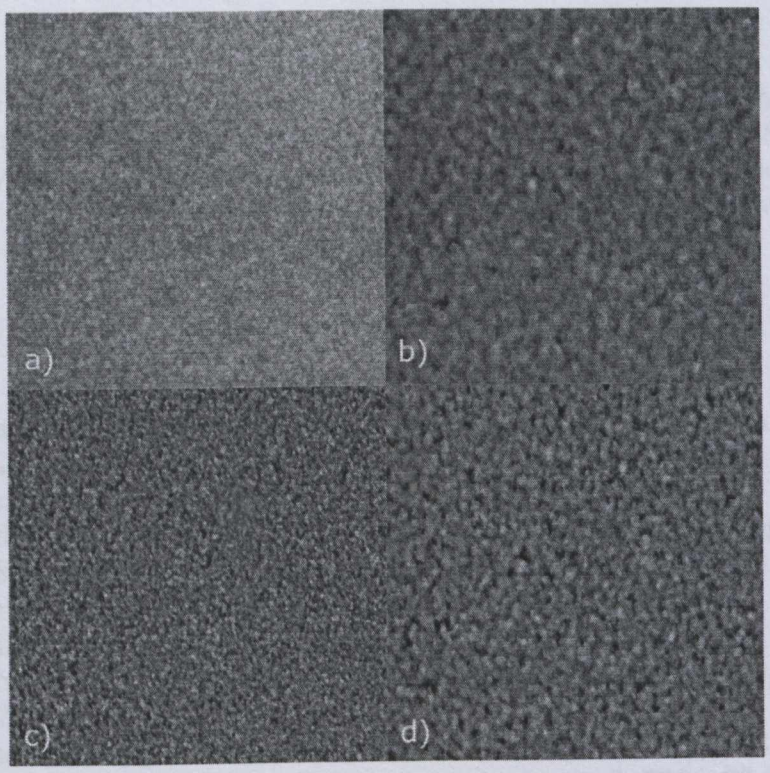


Figure 5. POM texture of Polymer (P-1). a. Nematic phase appeared below isotropic temperature (175.5 °C), b. Clear texture of nematic phase at 130 °C, c. Smetic A phase appeared at 110 °C, d. clear texture of Smetic A phage at 40 °C.

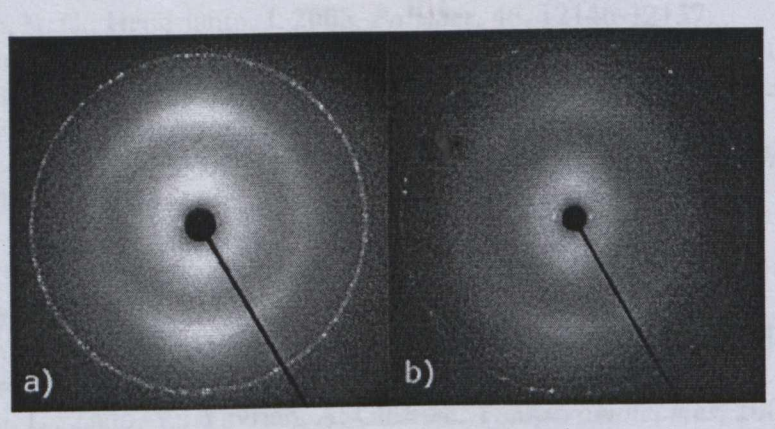


Figure 6. Smetic A phageWAXD image of Polymer (P-1)- a. at root temperature (26.5 Å), b. at 100 °C (26.8 Å).

Conclusions

In this study, a new polymerizable monomer containing naphthalene ring in the mesogens (M-1) was successfully synthesized. Different molecular weights of SCLCPs were synthesized by living ATRP of the synthesized monomer M-1. The synthesized SCLCP (P-1) showed a very wide range nematic phage, which is usually showed interesting viscoelectric behavior under share orientation.

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